



Canadian Patent

Brevet canadien

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To all to whom these presents shall come:

Whereas a petition has been presented to the Commissioner of Patents praying for the grant of a patent for a new and useful invention, the title and description of which are contained in the specification of which a copy is hereunto attached and made an essential part hereof, and the requirements of the Patent Act having been complied with,

Now therefore the present patent grants to the applicant whose title thereto appears from the records of the Patent Office and as indicated in the said copy of the specification attached hereto, and to the legal representatives of said applicant for a period of seventeen years from the date of these presents the exclusive right, privilege and liberty of making, constructing, using and vending to others in Canada the invention, subject to adjudication in respect thereof before any court of competent jurisdiction.

Provided that the grant hereby made is subject to the conditions contained in the Act aforesaid.

In testimony whereof, these letters patent bear the signature of the Commissioner and the seal of the Patent Office hereunto affixed at Hull, Canada.

A tous ceux qui les présentes verront:

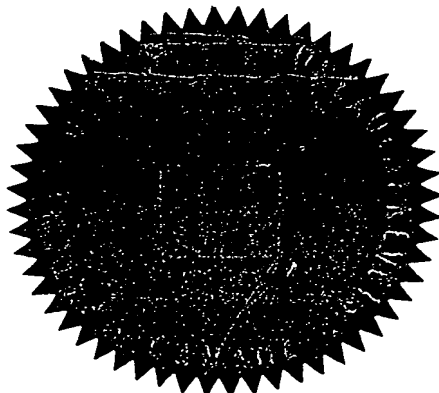
Considérant qu'une requête a été présentée au Commissaire des brevets, demandant la délivrance d'un brevet pour une invention nouvelle et utile, dont le titre et la description apparaissent dans le mémoire descriptif dont copie est annexée aux présentes et en fait partie essentielle, et que ladite requête satisfait aux exigences de la Loi sur les brevets,

A ces causes, le présent brevet confère au demandeur dont le titre de propriété audit brevet est établi d'après les dossiers du Bureau des brevets et est indiqué dans ladite copie du mémoire descriptif ci-annexé, et aux représentants légaux du dit demandeur, pour une période de dix-sept ans, à compter de la date des présentes, le droit, la faculté et le privilège exclusif de fabriquer, construire, exploiter et vendre à d'autres au Canada l'invention, sauf jugement en l'espèce par un tribunal de juridiction compétente.

La concession faite par les présentes étant soumise aux conditions contenues dans la loi précitée.

En foi de quoi ces lettres patentes portent la signature du Commissaire ainsi que le sceau du Bureau des brevets apposé à Hull, Canada.

FEB 26 1985



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(11) (A) No. **1 182 959**

(45) ISSUED 850226

(52) CLASS 18-16

(51) INT. CL. C08J 9/34³

(19) (CA) **CANADIAN PATENT** (12)

(54) Reverse Osmosis Membrane and Process for Making the
Same

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(21) APPLICATION No. 386,782

(22) FILED 810928

(60) SUPPLEMENTARY DISCLOSURE FILED 840229

(30) PRIORITY DATE U.S.A. (225,348) 810115

No. OF CLAIMS 36

Canada

REVERSE OSMOSIS MEMBRANE AND PROCESS
FOR MAKING THE SAME

BACKGROUND OF THE INVENTION

This invention pertains to new and improved membranes which are primarily useful in the treatment of water by reverse osmosis but which are also capable of other uses. The invention also pertains to the process of making such membranes.

In the purification of water by reverse osmosis, it is known that contaminated water is held under pressure against a
10 membrane having characteristics which are such that purified water accumulates on the side of the membrane remote from the contaminated water. Many different reverse osmosis membranes have been proposed and have been used to various different extents in the purification of water.

A reverse osmosis membrane should have certain desirable features. It should be comparatively easy and inexpensive to make. In addition, a satisfactory membrane of this type should be capable of withstanding the usual handling and storing prior to and during installation in a reverse osmosis apparatus
20 without physical damage or deterioration. Within such an apparatus a reverse osmosis membrane must present as low a resistance to the movement or flow of water from one side or surface of the membrane to the other as reasonably possible. Normally, the membrane must be capable of passing a significant quantity of water per unit time. In addition, the membrane should be capable of withstanding the pressure normally applied to the treated water and the pressure differential across the membrane without detrimental affect on the flow characteristics of the membrane.



A satisfactory reverse osmosis membrane must also not be affected by biodegradation and/or chemical reaction under the conditions or circumstances of use. The overall economics of a satisfactory reverse osmosis membrane require that, for some uses, the membrane be relatively satisfactory in removing contaminants, such as sodium chloride, from water, but in most applications, such membranes need not have to remove substantially all of such a contaminant from water. Water having a limited salt content may be tolerated and used, for example, by many plants and animals.

Prior art reverse osmosis membranes have not met all of the above-described criteria.

The search has continued for new and improved reverse osmosis membranes which meet the above-described criteria and solve these problems. This invention was made as a result of that search.

SUMMARY OF THE INVENTION

Broadly the present invention seeks to fulfill this need by providing new and improved reverse osmosis membranes. Thus, the invention seeks to provide reverse osmosis membranes as indicated in the preceding discussion: which are comparatively easy and inexpensive to manufacture; which are not apt to be damaged as a result of the normal handling and storage prior to and during their installation; which exhibit comparatively limited resistance to the movement or flow of water; which are capable of withstanding the pressures normally encountered during their use; and which are not damaged by either biodegradation or chemical reaction in the usual or normal conditions or circumstances of their use.

Accordingly, one aspect of this invention provides a reverse osmosis membrane, this membrane including an active layer and a physical support for the active layer, in which the

improvement comprises: the active layer consisting essentially of a continuous, non-porous film of an organic, film-forming polymer composition which is substantially inert in the presence of an oxidizing agent having a sufficient oxidizing potential to serve as a sterilizing agent. The film is from about 50 to about 1500 Å thick and is capable of dissolving an amount of water equal to at least two percent by weight of the film.

Another aspect of the invention pertains to a reverse osmosis membrane which includes an active layer and a physical support for the active layer. The improved membrane comprises a continuous, non-porous layer of an irreversible hydrogel composition containing at least one hydrogel-forming polymer and water, with the hydrogel layer being located between the support and the active layer. A reverse osmosis membrane of the present invention preferably utilizes as a support for the active layer an asymmetric layer or member of a relatively rigid or stiff character in which the porosity increases in accordance with the distance from a specific surface of the support layer or membrane. This surface of the support holds and is preferably bonded to a hydrogel layer serving several functions. It physically supports the active layer and in addition it serves to facilitate movement of water from the entire surface of the active layer to the pores in the support layer. This latter is beneficial in increasing the flow through the entire membrane.

This invention is also intended to provide a new and improved process for the manufacture of reverse osmosis membranes as are indicated in the preceding discussion. More specifically it is intended to provide a process as hereinafter indicated which may be easily and conveniently carried out at a comparatively nominal cost and which is especially desirable because of the physical characteristics of reverse osmosis

membranes as are produced by this process.

In accordance with this invention those objectives indicated in the preceding discussion pertaining to a process are achieved by providing in a process for producing a reverse osmosis membrane in which an active layer capable of dissolving water is located on a surface of a porous support the improvement which comprises: applying to said surface of said porous support prior to the location of said active layer on said surface of said porous support a water containing
10 solution of prepolymer chains capable of reacting so as to form an active layer, thereafter concurrently reducing the solvent content of said solution and reacting said prepolymer chains so as to form said active layer, the viscosity of said solution, the time and manner of said contact of said solution with said surface and the rate and conditions of said solvent removal being such that said active layer is formed on said surface of said support without penetration of said active layer into the pores of said support to an extent sufficient to significantly affect the ability of water to flow through
20 said support.

The invention further pertains to a process of producing a reverse osmosis membrane in which an active layer capable of dissolving water is located on a surface of a porous support. The improvement comprises applying to the surface of the porous support a water containing solution of prepolymer chains capable of reacting so as to form an active layer, and thereafter concurrently reducing the solvent content of this solution, and reacting the prepolymer chains so as to form the active layer. The viscosity of the solution, the time and manner of the contact
30 of the solution with the surface, and the rate and conditions of the solvent removal is such that the active layer is formed

on the surface of the support without penetration of the active layer into the pores of the support to any extent sufficient to detrimentally affect the ability of water to flow through the support.

Preferably the hydrogel layer reacts with the support as it is created so as to be cross-linked with the support. Similarly, preferably the active layer is cross-linked to the hydrogel layer as it is created.

BRIEF DESCRIPTION OF THE DRAWING

10 The present invention is more readily explained by reference to the accompanying drawing which is a diagrammatic, not to scale, cross-sectional view showing the essential character of a presently preferred embodiment or form of a reverse osmosis membrane in accordance with this invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

 In the drawing there is shown reverse osmosis membrane 10 in accordance with this invention which includes porous support 12 having surface 14 supporting hydrogel layer 16. This layer 16 has further surface 18 remote from support 12 which in turn
20 carries and physically supports active layer 20. If desired, numeral 14 may be considered as designating the surface of layer 16 adjacent to support 12. Similarly, numeral 18 may be considered as designating the surface of layer 20 adjacent layer 16. Support 12 may be referred to as a support layer or member. Support 12 may be reinforced by another support (not shown) if this is desirable for mechanical reasons.

 Within the broadest aspects of the present invention, support 12 may be any porous member physically capable of supporting layers 16 and 20. Thus, support 12 may

consist of a layer or sheet of paper, a layer or sheet of a felted, woven, knitted fabric or a layer or sheet of a perforated material. It will, of course, be recognized that such layers or sheets are known and are capable of being utilized for mechanical filtration purposes.

Although any such layer or sheet may be used with this invention, support 12 should preferably provide a minimum resistance to fluid flow from surface 14 to another surface 22 to support 12. Within limits it is possible to reduce the
10 resistance to fluid flow through support 12 by increasing the number of pores within support 12 and by increasing the relative sizes or dimensions of these pores. When carried to an extreme, however, expedients of this type are self-defeating since to be effective as a support, support 12 must have sufficient mass to hold layers 16 and 20 so that they are not likely to become physically damaged.

Since layers 16 and 20 must be as thin as reasonably possible in order to minimize their resistance to fluid flow, the pores in support 12 must be relatively small in order
20 to minimize the chance of damage to layers 16 and 20 when membrane 10 is subjected to a fluid pressure differential. Also, in order to minimize resistance to fluid flow these pores should be as "short" as possible. However, the lengths of the pores cannot be minimized to the point at which support 12 becomes so weak that it is unable to exercise its supporting function.

Accordingly, support 12 preferably has a physical character as indicated diagrammatically in the drawing. This support 12 is an asymmetric support in which surface 14 is essentially a film permeated by a multitude of small holes or pores 26. The material

within support 12 is "arranged" in a manner somewhat suggestive of the manner in which arches are utilized in many churches and similar buildings so that surface 24 of support 12 is essentially of an open character and only is intersected by sufficient material in post or pillar-like form so that support 12 can adequately serve its function. Between surfaces 14 and 24 both the material content and the porosity of support 12 vary with distance.

Pores 26 should preferably cover from about 10 to about 10 30 percent of the area of surface 14 and for from about 70 to about 95 percent of the surface area of surface 22 to be open. Thus the preferred support 12 used with the present invention may be described as an asymmetric layer, film or membrane containing on one surface from about 10 to about 30 percent open area and, on the other surface, from about 70 to about 95 percent open area. The amount of open area gradually changes in accordance with the distance between these two surfaces.

Pores 26 on surface 14 should be sufficiently small so that there is no tendency of layers 16 and 20 to collapse into 20 or rupture adjacent to these pores during the use of membrane 10. On the other hand, if pores 26 are too small they tend to impede flow through support 12. Accordingly, it is preferred that holes or pores 26 in surface 14 should be at least about 0.05 microns in diameter and should be no greater than about 0.5 microns in diameter. This maximum dimension is related to the characteristics and dimensions of layers 16 and 20 and may be varied somewhat in accordance with the changes in these layers

16 and 20 permissible within the scope of the present invention. The minimum figure is based upon flow control considerations which are substantially unrelated to the character of layers 16 and 20.

The thickness of a preferred support 12 in accordance with the present invention may also be varied between comparatively wide limits. Regardless of whether or not support 12 is asymmetric in character as indicated in the preceding discussion, it must contain sufficient mass so as to
10 be capable of physically supporting layers 16 and 20 so that these layers will not be damaged during use of membrane 10 and during normal handling. The amount of material required to attain a desired reinforcement may be readily determined by routine experimentation and will vary somewhat depending upon whether or not an auxiliary support (not shown) is used with support 12 and depending upon the properties of the material within support 12.

An integral asymmetric support 12 is best formed of an appropriate relatively "stiff" polymer, preferably a polymer of
20 a relatively rigid character having a glass transition temperature above about 130°C. so as to be sufficiently rigid in character to be resistant to collapse or deformation. Such deformation would tend to close or block off pores 26 when membrane 10 is subjected to a pressure differential in use.

It is preferred that support 12 be at least about 40 microns thick when used with an auxiliary support (not shown) which is capable of mechanically supporting support 12. When no such auxiliary support is used, it is preferred that support 12 be at least about 100 microns thick. If support 12 is substantially
30 thinner than indicated, it may rupture due to the presence of a

fluid pressure differential during use of membrane 10.

Normally, support 12 should not be more than about 20 microns thicker than either of these values since it would then present undesirable resistance to fluid flow.

Support 12 is preferably formed from a conventional or known polysulfone or polyamide polymer, although other polymers may also be used. Such polymers are relatively rigid and stiff and may be easily formed into supports corresponding to the preferred support 12. Further, such materials may be reacted so as to be cross-linked with hydrogel layer 16 as hereinafter described.

The support for the reverse osmosis membranes of the present invention is also preferably highly asymmetric as disclosed in applicant's Serial No. 372,460, filed March 6, 1981, and entitled "IMPROVED ASYMMETRIC MEMBRANES AND PROCESS THEREFOR". Membranes as disclosed in that application contain a skin and porous structure, the skin containing pores which have an average pore diameter of from about 0.005 to about 3.0 microns. The substructure comprises a reticulated structure which contains pores having an average pore diameter of from about 10 to about 20,000 times as large as the average pore diameter of the pores of the skin, the pores of the support increasing gradually in size from the skin to the face of the membrane opposite the skin. Such asymmetric support has a bulk porosity greater than about 70%.

Hydrogel layer 16 is a gel or gel system which may be based upon an inorganic material such as alumina or silica. In particular, hydrogels of the present invention are based upon water swollen random coils of polymer chains which are water loving in the sense that they tend to take up water so that there is some water "bound" in the polymer coils and some "free" or unbound water between the swollen polymer chains.

10 The polymers which are utilized to form such hydrogels are sometimes referred to as hydrocolloids or hydrocolloid-like polymers. Polyacrylic polymers, diaminobutane polymers and compounds such as alginic acid, guar gum and the like are commonly referred to as hydrocolloids or hydrocolloid-like polymers. In making layer 16, it is preferred to employ at least one hydrocolloid forming compound or polymer which is "lightly" cross-linked so as to improve the mechanical stability of layer 16. Since compounds such as alginic acid which are cross-linked utilizing ionic bonds are relatively sensitive to minor changes in pH in the sense that a comparatively minor change in pH will normally cause a resultant change in the physical properties of the hydrogel of such a compound, it is preferred to utilize polymers and compounds which are cross-linked to a lesser extent utilizing covalent linkages.

20 The molecular weight of a polymer or compound used to form a hydrogel utilized in layer 16 is important. If the polymer chains were too large, the viscosity of a solution containing such polymer chains would become so great as to make it difficult to utilize this solution in manufacturing layer 16. Furthermore, if these chains were too large, the process of manufacturing layer 16 would be unnecessarily complicated due

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to shear degradation. On the other hand, if the molecular weight of these chains were too low, hydrogel layer 16 would penetrate or clog pores 26 of support 12 to an extent sufficient to detrimentally affect fluid flow through pores 26 as a result of the formation of layer 16 upon layer 12.

Although polymers or compounds having a molecular weight of from about 30,000 to about 5,000,000 may be used in making hydrogel layer 16, it is preferable to use polymers or compounds having a molecular weight of from about 500,000 to about 3,000,000. If desired, several of such polymers or compounds may be used in hydrogel layer 16. Hydrogel layer 16 may be made using at least one polymer which contains vinyl groups since such polymers may be readily cross-linked through the formation of covalent links as the hydrogel is formed, and since such polymers form gels or gel systems which are effective in conveying or conducting water. Alternatively, polymers containing hydroxyl groups which may be cross-linked by ester groups or containing carboxylic acid groups to form amide cross-links may also be used.

Hydrogel layer 16 has two functions: 1) it physically holds or supports layer 20 at or along surface 18, and 2) it serves to distribute water flow from layer 20 to pores 26 of support 12. In order for layer 16 to adequately serve its purpose of distributing water, the hydrogel system within this layer 16 should not be significantly affected by any temperature changes normally encountered in shipping and handling of completed membrane 10. Further, layer 12 should be capable of conveying or transporting water effectively at any normally encountered water temperature. Accordingly, layer 16 preferably

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should consist essentially of a thermally irreversible gel system.

The distributive function of hydrogel layer 16 may best be explained by indicating what would happen if layer 20 was located directly against surface 14 of support 12. If this were the case those portions of layer 20 directly adjacent to pores 26 would receive fluid from layer 20 while those portions of layer 20 in contact with surface 14 between pores 26 would be blocked off by the material at surface 14 so as to be unavailable for reverse osmosis purposes.

Hydrogel layer 16 prevents this blocking effect because of the ability of a hydrogel to transmit or convey water. Hydrogel layer 16 is used with the present invention to conduct water from all portions of layer 20 in contact with surface 18 to pores 26 in surface 14. Thus this hydrogel layer 16 avoids what may be referred to as "dead spots" along surface 18. For hydrogel layer 16 to carry out this distributive function effectively, it must be sufficiently thick to distribute or conduct fluid from layer 20 to pores 26. It must also be sufficiently thick so as to be continuous or non-porous so as to completely support layer 20. On the other hand, layer 16 should not be so thick as to provide any substantial or excessive resistance to liquid flow from layer 20 to support 12 other than such resistance as is inherently necessary in distributing liquid from all portions of surface 18 to pores 26. Layer 16 should preferably be about as thick as the average distance between pores 26.

Accordingly, layer 16 should have a dry thickness of from about 0.1 to about 5 microns. If layer 16 is substantially thinner than about 0.1 micron, there is some danger that it will

be of a discontinuous character and it probably will not be thick enough to adequately transport and convey water. If, on the other hand, layer 16 is substantially thicker than 5 microns, more hydrogel will be present than is needed to perform the hydrogel functions, and the excess hydrogel will tend to interfere with water flow. Hydrogel layer 16 has a dry thickness of preferably from about 2 to about 3 microns since such a hydrogel layer adequately performs its intended functions and is normally free of any defects such as discontinuities.

10 Since the polymer chains in a hydrogel tend to swell in the presence of water or water and another appropriate solvent, the "wet" thickness of hydrogel layer 16 is greater than its dry thickness. This fact should be noted since on occasion reverse osmosis membrane 10 may be supplied with hydrogel layer 16 substantially depleted of liquid.

 The amount of swelling is dependent upon the specific polymer used in creating hydrogel layer 16. Such a polymer must be capable of taking up an amount of water equal to at least 150 percent of the weight of the polymer present when
20 layer 16 is at ambient pressure and temperature if the hydrogel is to be able to convey water at a desirable rate. Preferably the amount of water within layer 16 is at least 15 times the weight of polymer present under the noted conditions for the water to have a desired degree of mobility within layer 16. If layer 16 contains an amount of water substantially in excess of about 200 times the weight of the polymer under the noted conditions, hydrogel layer 16 will not normally possess the physical properties necessary for it to perform the functions discussed hereinabove.

30 Several other considerations should be noted in connection

with hydrogel layer 16. Preferably the polymer chosen for use in the formation of the hydrogel should be such that the hydrogel is not significantly affected by pressures such as will normally be encountered during use of membrane 10. Preferably the gel type structure formed will not be broken down or damaged at such pressures.

10 The pressure applied to membrane 10 during use may affect layer 16. In general, the greater the pressure applied to membrane 10 the greater the extent to which hydrogel layer 16 will tend to be compacted. The more layer 16 is compacted the greater the resistance of layer 16 to water flow through it and the greater the chance that some minor amount of water may be expressed from layer 16.

20 Active layer 20 is critical to the operation of reverse osmosis membrane 10 because it is this layer which normally completely performs the actual separation achieved in any reverse osmosis procedure. In order to achieve this separation with water, layer 20 must be hydrophilic so as to be capable of dissolving the water and thus segregate the dissolved water from other materials in the solution being purified which will not go into solution to any significant extent in the polymer in active layer 20. The active layer should be capable of absorbing generally at least about 2, typically from about 2 to about 20, and preferably from about 5 to about 15 percent by weight water on the basis of its own dry weight.

30 Generally, the greater the degree of water absorption by layer 20 the better since the easier it would be for water to move through this layer and, hence, the greater the flow which may be achieved through membrane 10. However, salt penetration into layer 20 tends to increase with an increase in water absorption. If layer 20 absorbs beyond about 20 percent by

weight of water on the basis of its own weight, layer 20 will tend not to be as selective as normally desired in achieving purification. If an amount of water substantially less than about 2 percent by weight of the dry polymer is absorbed by layer 20 during use of membrane 10, flow through membrane 10 is so limited as to make it unsuitable for most normal uses.

The ability of layer 20 to absorb water should be considered in connection with another factor. The thicker layer 20, the more "difficult" it is for it to conduct or transmit comparatively high quantities of water during membrane use. On the other hand, if layer 20 is undesirably thin, there is a limited danger that it may contain surface discontinuities or imperfections and thus not have a smooth, continuous, uniform character which is desirable in obtaining a consistent "purification" of water during use of membrane 10. Thus, layer 20 may be generally from about 50°A to about 1500°A thick. Preferred results are achieved, however, when layer 20 is from about 200°A to about 500°A thick.

Unless water to be purified using membrane 10 has been previously treated to kill any and all microorganisms, layer 20 will be exposed to those microorganisms. Since polymers of a hydrophilic, water dissolving character normally are either susceptible to attack as a result of growth of microorganisms on such polymers or susceptible to clogging as a result of microorganisms growing on the surface of such

polymers, it is disadvantageous to use membrane 10 with water which has not been treated to kill microorganisms present within such water.

Although it is, of course, possible to treat water in many different ways in order to kill microorganisms, as a practical matter there is only one way which is normally economic for killing microorganisms in water. This method involves treating water with an oxidizing agent having an oxidation potential sufficient to serve as a sterilizing agent for the water. Chlorine is the most commonly utilized sterilizing agent although ozone, and to a lesser extent other agents, such as iodine and various chlorine containing compounds, may also be used. Since such oxidizing or sterilizing agents must normally be used, the polymer utilized in layer 20 should be substantially inert in the presence of an oxidizing agent having an oxidation potential sufficient to serve as a sterilizing agent.

Furthermore, because water from many different sources also contains various enzymes such as cellulase which will not be significantly affected by oxidation treatments such as are normally utilized to kill various microorganisms, the polymer utilized in layer 20 should also be substantially inert in the presence of any enzyme which may be reasonably expected to be found within the water.

Normally only layer 20 need possess such inertness to an oxidizing agent and to the various enzymes discussed above. In using membrane 10, layer 20 serves essentially as a barrier which isolates both the material in hydrogel layer 16 and the material in support 12 from any oxidizing agent and any

enzyme present within the water. Even if some of the oxidizing agent or some enzyme within the water being treated should contact layer 16 or support 12, the chance of such contact causing any damage which would significantly detrimentally affect the operation of membrane 10 is quite limited.

10 Even if layer 16 or support 12 should become damaged as a result of contact with such an oxidizing agent or enzyme, this will not normally affect the operation of membrane 10 since it is layer 20, not layer 16 or support 12, which accomplishes the salt separation which is the purpose of this membrane.

Comparatively few organic polymers possess a degree of stability and a hydrophilic character as discussed above and are also capable of being applied to layer 16 in creating layer 18 without causing damage to layer 16. Epoxy, pheonolic, and partially hydrolyzed polyvinyl ester polymer or polymer system are preferred for use in layer 20 since such polymers are generally adequately resistant to oxidation and to enzyme attack, are sufficiently hydrophilic to be used in separating water, and may be applied to layer 16 without damaging it while membrane 10 is manufactured. 20 However, it is noted that not all polymers of these classes are useful for layer 20.

Generally, the desired degree of inertness in layer 20 results from the selection of a precise structural formula of the polymer or polymer system used in creating layer 20. Furthermore, the suitability of a particular polymer for use in layer 20 may generally be determined on the basis of routine testing in order to determine if such a polymer possesses 30

the various desirable characteristics indicated hereinabove. Epoxy, phenolic and partially hydrolyzed polyvinyl ester polymers are normally desired for use in layer 20 but even these polymers may not be desirable if they contain various reactive groups which may be chemically attacked by an oxidizing agent or enzyme.

Generally, any polymer useful in layer 20 should contain ester, vinyl or tertiary amide cross-links in the polymer. Furthermore, any useful polymer of the epoxy type should have
10 exposed carboxylic acid groups. Furthermore, any epoxy, phenolic, or partially hydrolyzed polyvinyl ester should only contain hydroxyl groups which are spaced or remote from electron donor or electrophilic groups and any halogen or other hydroxyl groups present in the polymer chain.

The epoxy resins useful in this invention may be formed by cross-linking prepolymer chains having terminal hydroxyl groups with tetrafunctional carboxylic acids and anhydrides to produce polymers containing ester cross-linkages and exposed
20 carboxylic acid groups. Generally, phenolic polymers may be obtained by cross-linking conventional commercially available resol and novolak or phenoxy resins with difunctional acid anhydrides such as maleic, phthallic and various similar difunctional anhydrides.

The partially hydrolyzed polyvinyl esters useful in this invention may be produced by partially hydrolyzing polymers, such as polyvinyl acetate or butyrate resins, to an extent sufficient to attain a desired degree of salt rejection as well as satisfactory ability to "transmit" water.

In general, a polyvinyl ester which is from about 10 to about 50% hydrolyzed is satisfactory for use in this invention. If such a polymer is hydrolyzed to an extent substantially greater than about 50% it will not exhibit the desired degree of salt rejection. If it is hydrolyzed substantially less than about 10%, it will not exhibit the desired ability to absorb water. Whenever the expression "partially hydrolyzed polyvinyl ester" is used in this specification or claims, it designates a polymer which has been hydrolyzed in an amount as noted.

10 The reverse osmosis membranes of the present invention may be manufactured in a number of different, somewhat related manners. When this membrane uses a conventional or known support as support 12, one must first locate layer 16 upon support 12 and then subsequently locate layer 20 on layer 16. Because layers 16 and 20 are quite thin they cannot normally be separately manufactured and then deposited in place at a reasonable cost, but must be formed in situ. Thus, layer 16 must be formed upon layer 12 and then in turn layer 20 must be formed upon layer 16. By utilizing entropic segregation as indicated
20 hereinbelow, these layers 16 and 20 may be concurrently produced.

 Generally, layers 16 and 20 may be created utilizing known or conventional techniques for creating comparatively thin continuous films or coatings. Thus, layers 16 and 20 may be formed by preparing appropriate solvent solutions and then depositing these solutions by known or conventional roller, transfer, brush, wick or dip coating techniques. Any such deposition of solution must, of course, be followed by solvent removal, either by air drying or by heating at a temperature sufficiently low as to avoid polymer damage but sufficiently
30 high as to cause some cross-linking between polymer chains.

As a result of depositing layer 16 upon support 12 and layer 20 upon layer 16, there will be some degree of physical interlocking resulting from the intimate physical contact at surfaces 14 and 18 which will tend to hold support 12 to layer 16 and layer 20 to layer 16 to an adequate extent for most purposes. In some cases, however, this physical holding action may not be adequate to prevent some separation or movement between support 12 and layer 16 and between layer 20 and layer 16. For this reason, support 12, layer 16, and layer 20 are all preferably cross-linked so as to achieve a type of chemical bond at each of surfaces 14 and 18. Such cross-linking may be achieved by utilizing appropriate polymers or polymer systems capable of cross-linking.

As indicated hereinabove, support 12 preferably consists essentially of a polysulfone, or polyamide polymer having a particular type of asymmetric physical structure. This support 12 may be manufactured by forming a solution of the polymer and then casting this solution onto an imporous transfer sheet such as, for example, a stainless steel belt to a desired thickness capable of resulting in the production of a support 12 having a particular desired thickness. Thereafter, the exposed surface of the film located on the imporous sheet may be quenched in water, preferably deionized or distilled water, at ambient temperatures. The support may then be removed from the transfer sheet. This results in the production of support 12 having a preferred physical structure as indicated hereinabove. Preferably support 12 is then washed several times with deionized or distilled water to remove any vestiges of the solvent employed in preparing the polymer solution.

Support 12 produced in this manner may or may not contain reactive groups capable of cross-linking with the polymer or polymer system used in a hydrogel layer 16. When cross-linking between support 12 and hydrogel layer 16 is desired, the surface of the support may be treated to modify the polymer in order to place reactive groups on the surface of the polymer. One manner in which this may readily be accomplished with a polymer such as a polysulfone is to treat the surface of the polymer with a hydrogen peroxide solution under such conditions as to modify the surface of the polysulfone so that the surface contains sufficient hydroxyl groups to effectively cross-link to or with subsequently created hydrogel layer 16. Other treatments designed to accomplish the same type of objective may also be used. Thus, the surface of a polysulfone support may be treated with a very dilute solution of chlorosulfonic acid for a brief period to produce the sulfonic acid groups capable of forming cross-links.

As indicated above, care should be taken in preparing hydrogel layer 16 in order to substantially avoid the penetration of hydrogel 16 within pores 26 in surface 14 of support 12. This penetration is substantially avoided or minimized preferably by applying an extremely dilute solution of a hydrogel forming polymer of a molecular weight as indicated hereinabove and then removing solvent under such conditions that there is minimal penetration of the solution within pores 26. In general, the higher the viscosity of the solution the less chance of penetration.

Because the hydrogel forming polymer within such a solution is swollen by the solvent or solvent system used to as great an extent as reasonably possible and the solvent solution of the hydrogel polymer coils is quite dilute, several important benefits are achieved. One such benefit is that the solution of the hydrogel polymer coils may be readily handled as a liquid so as to be readily applied by techniques discussed hereinabove. Another benefit is that the swollen polymer coils within the solution are large enough that the solution is sufficiently
10 viscous so that it will not readily penetrate pores 26 within surface 12 and thus not clog or block these pores.

Surface 14 of support 12 may be considered more or less as a common filter in filtering solids out of a liquid by tending to hold back swollen polymer coils on surface 14 so that such coils will constitute layer 16 as solvent is removed.

The penetration of such solution into pores 26 may be minimized through the use of a viscosity controlling agent which is sufficiently inert so as not to affect the operation of layer 16 or which will be expelled from layer 16 during its
20 final stages of formation and readily removed during rinsing. Thus, for example, a common high molecular weight polyethylene glycol having wax-like characteristics may be used in the amount of 2 or 3% by weight of the total weight of the polymer or polymer system in hydrogel layer 16 so as to increase the viscosity of the hydrogel polymer solution. The use of such a

viscosity controlling agent is preferred in aiding the formation of a continuous hydrogel layer.

Generally, if the molecular weight of the polymer coils in a hydrogel solution is undesirably low, there is a tendency for a dilute solution not to form a continuous film when applied by conventional techniques. To a degree this tendency may be combatted through the use of a viscosity controlling agent as indicated hereinabove. On the other hand, in general, the lower the molecular weight of the polymer coils in hydrogel layer 16 the more this layer will tend to penetrate pores 26 within surface 14 of support 12.

If the molecular weight of the hydrogel polymer coils is sufficiently low, there will be a tendency for such pores to fill or become clogged with hydrogel layer 16 due to penetration of the hydrogel solution even when a viscosity controlling agent is employed. Thus, the solvent or solvent system may contain very minor amounts of wetting agents which will tend to promote uniform spreading of the hydrogel forming solution.

The solvent or solvent system employed in producing hydrogel layer 16 should be of such a nature as to avoid any sort of "action" with respect to support 12. Thus, for example, that solvent or solvent system is preferred which does not significantly tend to swell any polymer within support 12. If the solvent or solvent system tends to dissolve or significantly swell the polymer in support 12, there is danger that the desired porosity within support 12 may be detrimentally affected and this, in turn, would detrimentally affect the flow characteristics of membrane 10.

Thus, when support 12 is of a preferred polysulfone or

polyamide, the solvent or solvent system should consist of water or a mixture of water with a lower aliphatic alcohol (C_1 to C_8 inclusive) such as, for example, isopropyl alcohol. The water is, of course, required in order to form a hydrogel. Both it and the lower aliphatic alcohol may readily be removed from layer 16 as it is being formed.

10 Thus, for example, the solution used in forming hydrogel layer 16 may be prepared by first dissolving in a solvent the particular polymer or polymers which preferably contain at least two reactive sites capable of being used in forming covalent cross-links at each of their ends. When this polymer is cross-linked in solution, a hydrogel forming polymer is formed which has a desired stability against weakening of the solution by heat--i.e., there is produced a thermally irreversible gel.

20 The presence of reactive sites on the hydrogel polymers is also beneficial for other reasons. Because of the dilution of the solution needed to form hydrogel layer 16, there is usually adequate reactive sites on the hydrogel polymers for two different types of cross-linking to occur. When support 12 contains these reactive sites, these reactive sites form covalent bonds with the reactive sites in the hydrogel polymer material of layer 16 during deposition and solvent removal.

30 Furthermore, additional cross-linking between the reactive sites of support 12 and the polymer coils of the hydrogel material may take place as layer 16 is formed and solvent is removed from it. This is desirable since it tends to increase the physical strength of hydrogel layer 16. Thus, it is preferable to select the hydrogel forming polymer or polymers

so that not all functional sites capable of cross-linking are reacted prior to the creation of the final active layer 20.

The procedure normally followed in forming active layer 20 reasonably corresponds to the procedure previously described in connection with the formation of layer 16. This procedure involves forming a solution, depositing the solution, and then removing the solvent from the solution as well as the other details set forth hereinabove.

10 In order to prevent and/or minimize the chances of damage to either layer 16 or support 12 it is preferred to utilize a solvent or solvent system as previously described in connection with the creation of layer 16 which consists of water, a lower aliphatic alcohol (C_1 to C_8 inclusive), or a mixture of the two. Because such a solvent or solvent system is the same as that used in the formation of hydrogel layer 16, there is substantially no chance of damage to the hydrogel layer 16 as a result of the use of this solvent or solvent system.

20 This solvent or solvent system is utilized in connection with layer 16 because it does tend to dissolve or swell the preferred polymer used in forming support 12. If support 12 is resistant to the solvent, however, it may be used in forming layer 20 provided it also does not damage layer 16. For example, chloroform may be used if support 12 is made of a polyester or polyamide.

30 There is, however, a problem associated with the use of any such solvent or solvent system. The polymers which are capable of being used in forming layer 20 tend to be relatively difficult to dissolve in the solvent or solvent system. This is particularly the case when the molecular weights of such polymers are as high as is normally desired in connection with layer 20 and when the polymers are epoxy or phenolic.

Because of this problem, the solution used in forming layer 20 consisting of an epoxy or phenolic polymer will also contain prepolymer chains of comparatively low molecular-weight which have to be further reacted with one another to form active layer 20 having the ultimate physical properties.

When it is desired to utilize an epoxy layer 20, the solution employed will, because of the solubility problem noted, normally contain prepolymer chains having 1) terminal hydroxyl groups which are sufficiently short so as to readily dissolve in the solvent or solvent system, and 2) tetrafunctional carboxylic acid anhydrides of a similar solubility. As previously indicated, for a phenolic layer 20 such chains may be novolak or phenoxy resins. In forming final polymer layer 20 of a phenolic resin it is normally considered necessary to incorporate within the solution a comparatively small, but effective, amount of a hardener and/or a catalyst in accordance with conventional practice. These materials are necessary in promoting the desired actions in forming the final active polymer within a comparatively limited time period at a comparatively moderate temperature.

Suitable curing agents or hardeners are various divalent acids and divalent acid anhydrides such as maleic, phthalic and other similar acids which are conventionally used for this purpose. Conventional catalysts, such as boron trifluoride, various quaternary phosphonium alkyl or aryl compounds, benzoyltrimethylammonium iodide, zinc stearate, N,N-diethanolamine and the like may be conveniently utilized. Generally, it is preferable to utilize amounts of a curing agent and a catalyst which are effective in forming the desired hydrophilic polymer under such conditions that no damage will occur to either support 12 or layer 16 as a result of undue heating or the like. The curing

agents, catalyst, and prepolymer chains used to form a phenolic layer 20 must, of course, be selected with reference to their solubility in the particular solvent or solvent system employed.

The solution used in forming an epoxy or phenolic layer 20 is preferably sufficiently dilute so that there is substantially no chance of the prepolymer chains present in the solution reacting until the solvent content of the solution is reduced as, for example, by evaporation during drying of the solution after it is applied to layer 16. The precise amount of solvent or solvent
10 mixture needed may be determined by routine experimentation. An excess over the amount needed is preferably employed so as to avoid any possibility of an undesired reaction.

It is possible to produce membrane 10 having separate hydrogel layer 16 and separate active layer 20 concurrently by making use of entropic segregation. In concurrently producing two such layers 16 and 20 a solution is prepared utilizing a solvent or a solvent system such as is used in connection with the separate preparation of either of these layers. This solution should contain both swollen hydrogel polymer coils and various specific
20 "ingredients" as identified hereinabove for the production of active layer 20. Such a solution should be applied to support 12 and then heated at a temperature sufficient to volatilize the solvent present and to cause appropriate reactions leading to the formation of active layer 20 and hydrogel layer 16. Such heating conditions should normally be sufficiently effective to cause any cross-linking which is possible between the functional groups of the polymer forming ingredients. The solution utilized should be applied to support 12 in any conventional manner known to those skilled in this art.

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When the solution is heated, entropic segregation will take place to a significant extent. This segregation may be promoted by precise control of the heating used to remove the solvent and to cause reaction from the ingredients from within the solution applied to create layers 16 and 20. When layers 16 and 20 are produced in this manner, they are not as separate and distinct as when separately produced. To a significant extent, they are physically intermixed such that they are not readily separated. When layers 16 and 20 are produced in this manner, they are sufficiently effective in removing salt from salt water so as to provide water which is sufficiently salt free to be useful in many different non-critical applications where extreme water purity is not required. When extreme water purity is required, however, layers 16 and 20 should be separately produced.

The present invention is illustrated by the following examples. All parts and percentages in the examples as well as in the specification and claims are by weight unless otherwise specified.

EXAMPLE 1

Support 12 may be prepared by first preparing a solution of 11 parts polyarylsulfone in 14 parts methyl butanol and 75 parts dimethylformamide. This solution is cast at 30°C onto an inert, imporous transfer sheet such as, for example, a flexible belt coated with a polyethylene surface coating at a temperature of about 20°C. to a wet thickness of about 400 microns. The film produced in this manner is then quenched in distilled water at a temperature of about 20°C. for a period of about three minutes. Then the support is washed several times in distilled water and dried in air at about 160°C. for two minutes.

30

Next, a previously prepared solution of 1 part polyacrylic acid polymer having an average molecular weight of about 1,000,000 in 99 parts distilled water at 20°C. is coated on the surface of the support remote from the transfer sheet in a thickness as determined by experimentation to be adequate to form a hydrogel layer having a dry thickness of about two hundred microns. As soon as the polyacrylic acid solution is applied to the surface of the support, the support, including the wet film, is dried in a forced air oven at about 140°C. for a period of
10 about two minutes. Drying results in the production of a hydrogel layer corresponding to layer 16.

Active layer 20 is prepared by first preparing a solution of 0.4 parts epoxy resin having an average molecular weight of about 20,000 (Araldite 488), 0.1 parts pre-polymer of phenol-formaldehyde, water borne phenolic hardener, 0.001 part boron tri-fluoroethanate catalyst, 49.2 parts water, and 50.0 parts methyl alcohol at 20°C. This solution is then placed on the hydrogel layer. An excess of this solution over the amount which automatically adheres to the
20 hydrogel layer as a result of surface tension is applied to the hydrogel layer. The coated composite sheet is then held vertically for the time required for the latter coating to drain so as to establish its own surface thickness. As soon as this occurs, the composite, including the solution, is baked in air at 120°C. for five minutes to remove solvent and to cure the active film. The completed membrane is then removed from the transfer sheet.

EXAMPLE 2

The procedure of Example 1 is followed but instead of the inert, imporous transfer sheet of Example 1 there is used a

continuous sheet of paper sold under the trademark "PELLON 6800".

EXAMPLE 3

The procedure of Example 1 is varied so that the transfer sheet is removed from the support immediately following the air drying of the film which is converted into the support. Using this procedure, the support is not reinforced since a hydrocolloid layer and an active layer are produced on it.

EXAMPLE 4

10 The procedure of Example 1 is varied in connection with the production of the active layer. A solution containing one part of an A-stage or resol, one-step, thermosetting phenol-formaldehyde resin consisting primarily of partially condensed phenol alcohols in 99 parts water at room temperature is titrated to a pH of about 7 utilizing a 0.1N solution of sodium hydroxide. This solution is applied to the hydrogel layer instead of the solution used to produce the active layer in Example 1. After draining, the composite is air dried at 100°C. for a period of 10 minutes to produce the final membrane. This membrane is then removed from the transfer sheet.

20

EXAMPLE 5

The procedure of Example 1 is followed in the production of the support. Thereafter, hydrogel layer 16 and active layer 12 are formed by using a solution consisting of 1.8 parts of acrylic acid, 0.2 parts of an epoxy resin having an average molecular weight of about 25,000 (Araldite 6010) and 98 parts of ethanol. The solution is filtered and allowed to stand at room temperature for a period of one hour.

30 Thereafter, the solution applied to the exposed surface of the support utilizing a polyurethane foam coating wick so as to produce a layer of the solution having a sufficient thickness so

that, ultimately, a hydrocolloid layer of about 2.5 microns dry thickness and an active layer of about 350°A. results. Thereafter, the transfer sheet and the support holding-the applied solution are heated in an oven in air at about 120°C. for a period of about 10 minutes. This removes the solvent present and results in entropic segregation to the extent that the hydrocolloid layer and the active layer produced are reasonably separate and distinct from one another, although there is still an intermingling of these layers at the interface between them.

10

EXAMPLE 6

The procedure of Example 1 is varied by providing an additional step. This step concerns the treatment of the dry support prior to the application of the polyacrylic acid solution. The exposed surface of the support is treated with a solution containing 30 parts hydrogen peroxide, 0.02 parts of a conventional surfactant (FSN) and 69.98 parts water to which there has been added an amount of ferrous sulfate which is such that the solution contains 5 parts per million of ferrous sulfate. This solution is applied to the surface of the support at a temperature of 85°C. and is held in contact with this surface for a period of 10 minutes. Thereafter, the treated support is washed several times in distilled water and then air dried at 120°C. for a period of five minutes. The support treated in this manner contains hydroxyl groups which react with the polyacrylic acid during the subsequent step of Example 1 so as to form covalent cross-links.

20

EXAMPLE 7

The procedure of Example 1 is varied by providing an additional step which corresponds closely to the additional step set forth in Example 6. This additional step also concerns the

30

treatment of the dry support prior to the application of the polyacrylic acid solution. The exposed surface of the support is treated with a solution containing 0.1 parts of chlorosulfonic acid in 99.9 parts of hexane at room temperature for a period of about 20 seconds. Reaction is indicated by the formation of hydrogen chloride gas. This reaction produces sulfonic acid groups on the support which cross-link with polyalkylamine (Dow,™ Tydex 12) added during the subsequent step of Example 1 so as to form covalent cross-links. The chlorosulfonic acid used is washed from the surface of the support with distilled water prior to contact of this surface of the support with the polyacrylic acid solution.

EXAMPLE 8

The procedure of Example 1 is varied by utilizing a solution of a polyacrylic acid derivative polymer or prepolymer segments having a molecular weight of about 500,000 and having two vinyl groups attached to each polymer chain instead of the polyacrylic polymer specified in Example 1. All other details are as specified in Example 1. (This solution can be used instead of the polyacrylic acid polymer solution specified in any of the Examples indicated in the preceding discussion except Example 5.) During the drying of this polyacrylic acid solution, the polymer chains connect up with one another to a limited extent by the addition of a 0.01% potassium persulfate aqueous solution.

EXAMPLE 9

The procedure of Example 1 is varied so as to produce a membrane using a different active layer than is specified in Example 1. This alternate active layer uses a hydrolyzed poly-

vinyl acetate which is prepared by: (1) treating a commercial polyvinyl acetate polymer with a solution of 10 parts sodium hydroxide in 90 parts water at ambient temperature until about 50% of the polymer is hydrolyzed; (2) precipitating the hydrolyzed polymer from the solution with ethanol; (3) separating this polymer by filtration; (4) neutralizing the separated polymer with hydrochloric acid; and (5) washing and drying the polymer. This polymer is used by forming a solution containing 0.5 parts of it in 99.5 parts acetone and 0.025 parts pyromellitic anhydride. Promptly after being formed, the solution is spread on a hydrogel layer as specified in Example 1 to a thickness which will produce an active layer of a desired thickness after drying. It is then allowed to air dry. The final membrane is produced by heating in air at 120°C. for 10 minutes.

The principles, preferred embodiments, and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in this art without departing from the spirit of the invention.

SUPPLEMENTARY DISCLOSURE

In the disclosure as originally framed, it is stated that epoxy, phenolic and partially hydrolyzed polyvinyl ester polymer or polymer systems are preferred for use in layer 20 since such polymers are generally adequately resistant to oxidation and to enzyme attack, are sufficiently hydrophilic to be used in separating water and may be applied to layer 16 without damaging it while membrane 10 is manufactured.

10 A particularly preferred polymer for layer 20 is cellulose triacetate because of its resistance to chlorine, favorable water permeability, and very high salt retention. The cellulose triacetate is applied to the support preferably by dip coating the support in a very dilute (from about 0.1 to about 0.7% by weight) solution of cellulose triacetate in chloroform. The support may be submerged within the solution of cellulose triacetate via a roller submerged within the solution. When this preferred cellulose triacetate active layer is employed, polyvinylidene fluoride is the preferred support because it is compatible with the chloroform solvent and also because it
20 otherwise functions as a useful support.

EXAMPLE 10

More particularly, a preferred support is prepared by first dissolving 15 grams of polyvinylidene fluoride in 85 milliliters of dimethylformamide by stirring over a period of about 12 hours. This solution is then cast onto an inert, imporous transfer sheet which is a flexible belt with a polyethylene surface coating at 20°C. using a knife with a gap of 15 mils. The film produced in this manner is then quenched in distilled water at about 20°C. for a period of about 5 minutes. The
30 support produced as a result of these steps is then washed several times in distilled water and then dried in air at about 100°C. for a period of ten minutes.

Next, a previously prepared solution of 1 part polyacrylic acid having an average molecular weight of about 1,000,000 in 99 parts distilled water at 20°C. is coated on the surface of the support remote from the transfer sheet to a wet thickness which will ultimately result in a dry thickness of about two microns. As soon as the polyacrylic acid solution is applied to the surface of the support, the support, including the wet film, is dried in a forced air oven at about 140°C. for a period of about two minutes. This drying results in the production of a hydrogel layer corresponding to layer 16.

Active layer 20 is prepared by applying a 0.3% cellulose triacetate solution in chloroform to the polyvinylidene support by means of a polyurethane foam coating wick. The support stains with crystal violet dye but the thin film component does not produce a dye stain which illustrates the fact that the thin film is continuous.

The membrane is used to purify water containing sodium chloride. The sodium chloride rejection is 89%.

The above supplementary disclosure is simply a further exemplary embodiment of the principles of this invention, and the invention is not to be construed as limited to the particular forms disclosed since they are to be regarded as illustrative rather than restrictive.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A reverse osmosis membrane including an active layer and a physical support for the active layer in which the improvement comprises:

the active layer consisting essentially of a continuous, non-porous, uniform film of an organic, film-forming polymer which is substantially inert in the presence of an oxidizing agent having a sufficient oxidizing potential to serve as a sterilizing agent,

said film being from about 50 to about 1500 Å thick and being capable of dissolving an amount of water equal to at least two percent by weight of the weight of the film.

2. A membrane as claimed in claim 1 wherein: said membrane includes a continuous, non-porous layer of an irreversible hydrogel composition containing at least one hydrogel-forming polymer and water, said hydrogel layer being located between said support and said active layer.

3. A membrane as claimed in claim 2 wherein: said hydrogel layer is from about 0.1 to about 5 microns thick when dry,

said hydrogel forming polymer is capable of absorbing an amount of water equal to at least 150 percent of its own weight,

said polymer in said hydrogel layer being present in the form of swollen polymer coils of polymer chains of a molecular weight of from about 30,000 to about 5,000,000.

4. A membrane as claimed in claim 2 wherein: said hydrogel layer is from about 2 to about 3

microns thick when dry,

said polymer in said hydrogel layer is capable of absorbing an amount of water equal to at least 15 times the weight of said hydrogel forming polymer and is incapable of absorbing an amount of water in excess of about 200 times of its own weight,

said hydrogel forming polymer in said hydrogel layer is present in the form of swollen polymer coils of polymer chains of the molecular weight of from about 500,000 to about 3,000,000.

5. A membrane as claimed in claim 1 wherein: said film-forming polymer is a polymer selected from the group consisting of hydrophilic, partially hydrolyzed polyvinyl ester, epoxy and phenolic polymers.

6. A membrane as claimed in claim 5 wherein: said film-forming polymer is capable of absorbing an amount of water equal to from about 2 to about 20 percent of its own weight, and said film is from about 50 μ A to about 1500 μ A thick.

7. A membrane as claimed in claim 5 wherein: said film-forming polymer is capable of absorbing an amount of water equal to from about 5 to about 15 percent of its own weight, and said film is from about 200 μ A to about 500 μ A thick.

8. A membrane as claimed in claim 1 wherein: said membrane includes a continuous, non-porous layer of a thermally irreversible hydrogel composition containing at least one hydrogel-forming polymer and water, said hydrogel layer being located between said support and said active layer,

said film-forming polymer is a polymer selected from the group consisting of hydrophilic, partially hydrolyzed polyvinyl ester, epoxy and phenolic polymers.

5 9. A membrane as claimed in claim 8 wherein:
said hydrogel layer is from about 0.1 to about
5 microns thick,

 said hydrogel forming polymer is capable of ab-
sorbing an amount of water equal to at least 150
10 percent of its own weight,

 said polymer in said hydrogel layer being pre-
sent in the form of swollen polymer coils of polymer
chains of a molecular weight of from about 30,000 to
about 5,000,000,

15 said film-forming polymer is capable of ab-
sorbing an amount of water equal to from about 2 to
about 20 percent of its own weight, and said film is
from about 500A to about 1500A thick.

20 10. A membrane as claimed in claim 8 wherein:
said hydrogel layer is from about 1.5 to about
5 microns thick,

 said polymer in said hydrogel layer is capable
of absorbing an amount of water equal to at least 15
25 times the weight of said hydrogel forming polymer and
is incapable of absorbing an amount of water in ex-
cess of about 200 times of its own weight,

 said hydrogel forming polymer in said hydrogel
layer is present in the form of swollen polymer coils
30 of polymer chains of the molecular weight of from
about 500,000 to about 3,000,000,

 said film-forming polymer is capable of dis-
solving an amount of water equal to from about 5 to
about 15 percent of its own weight,

35 said film is from about 2000A to about
5000A thick.

11. A membrane as claimed in Claim 2,
wherein:

5 said support is a porous asymmetric member having a porous surface in contact with said hydrogel layer, the porosity of said asymmetric member increasing in accordance with the distance away from said hydrogel layer.

10 12. A membrane as claimed in claim 11 wherein:
from about 10 to about 30 percent of the surface of said support in contact with said hydrogel layer is open and from about 70 to about 95 percent of the surface of said support remote from said hydrogel layer is open.

15 13. A membrane as claimed in claim 11 wherein:
the pores within said porous surface in contact with said hydrogel layer are at least about 0.05 microns in diameter and are no greater than about 0.5
20 microns in diameter,

said pores in said surface in contact with said hydrogel layer being substantially free from material from within said hydrogel layer.

25 14. A membrane as claimed in claim 11 wherein:
said support is formed of a polymer having a glass transition temperature above about 130°C and is from about 40 to about 120 microns thick.

30 15. A membrane as claimed in claim 1 wherein:
said membrane includes a continuous, non-porous layer of a thermally irreversible hydrogel composition containing at least one hydrogel-forming polymer and water, said hydrogel layer being located
35 between said support and said active layer,
said hydrogel layer is from about 0.1 to about

5 microns thick when dry,

said hydrogel forming polymer is capable of absorbing an amount of water equal to at least 150 percent of its own weight,

5 said polymer in said hydrogel layer being present in the form of swollen polymer coils of polymer chains of a molecular weight of from about 30,000 to about 5,000,000,

10 said film-forming polymer is a polymer selected from the group consisting of hydrophilic, partially hydrolyzed polyvinyl ester, epoxy and phenolic polymers,

15 said film-forming polymer is capable of dissolving an amount of water equal to from about 2 to about 20 percent of its own weight,

20 said support is a porous asymmetric member having a porous surface in contact with said hydrogel layer, the porosity of said asymmetric member increasing in accordance with the distance away from said hydrogel layer,

25 from about 10 to about 30 percent of the surface of said support in contact with said hydrogel layer is open and from about 70 to about 95 percent of the surface of said support remote from said hydrogel layer is open,

the pores within said porous surface in contact with said hydrogel layer are at least about 0.05 microns in diameter and are no greater than about 0.5 microns in diameter,

30 said pores in said surface in contact with said hydrogel layer being substantially free from material from within said hydrogel layer.

16. A membrane as claimed in claim 1 wherein:
said membrane includes a continuous, non-porous layer of a thermally irreversible hydrogel composi-

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tion containing at least one hydrogel-forming polymer and water, said hydrogel layer being located between said support and said active layer,

5 said hydrogel layer is from about 2 to about 3 microns thick when dry,

 said polymer in said hydrogel layer is capable of absorbing an amount of water equal to at least 15 times the weight of said hydrogel-forming polymer and is incapable of absorbing an amount of water in
10 excess of about 200 times of its own weight,

 said hydrogel-forming polymer in said hydrogel layer is present in the form of swollen polymer coils of polymer chains of the molecular weight of from about 500,000 to about 3,000,000,

15 said film-forming polymer is a polymer selected from the group consisting of hydrophilic, partially hydrolyzed polyvinyl ester, epoxy and phenolic polymers,

 said film-forming polymer is capable of dissolving an amount of water equal to from about 5 to about 15 percent of its own by weight,

20 said film is from about 200° to about 500°A thick,

 said support is a porous asymmetric member having a porous surface in contact with said hydrogel layer, the porosity of said asymmetric member increasing in accordance with the distance away from said hydrogel layer,

25 from about 10 to about 30 percent of the surface of said support in contact with said hydrogel layer is open and from about 70 to about 95 percent of the surface of said support remote from said hydrogel layer is open,

30 the pores within said porous surface in contact with said hydrogel layer are at least about 0.5 microns in diameter and are no greater than about 5
35

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microns in diameter,

said pores in said surface in contact with said hydrogel layer being substantially free from material from within said hydrogel layer.

17. A membrane as claimed in claim 16 wherein:

said polymer coils are cross-linked within said hydrogel composition.

18. A membrane as claimed in claim 16 or 17 wherein:

said support is a polymer support,

said polymer coils are cross-linked to one another, to said support and to said active layer.

19. A membrane as claimed in claim 16 or 17 wherein:

said support is formed of a polymer having a glass transition temperature above about 130°C., is from about 40 to about 120 microns thick.

20. A membrane as claimed in claims 16 or 17 wherein:

said support is a polymer support,

said polymer coils are cross-linked to one another, to said support and to said active layer,

said support is formed of a polymer having a glass transition temperature above about 130°C., is from about 40 to about 120 microns thick.

21. A process of producing a reverse osmosis membrane in which an active layer capable of dissolving water is located on a surface of a porous support in which the improvement comprises:

applying to said surface of said porous support a water containing solution of prepolymer chains capable of reacting so as to form an active layer,

thereafter concurrently reducing the solvent content of this solution and reacting said prepolymer chains so as to form said active layer,

the viscosity of said solution, the time and manner of said contact of said solution with said surface, and the rate and conditions of said solvent removal being such that said active layer is formed on said surface of said support without penetration of said active layer into the pores of said support to any extent sufficient to detrimentally affect the ability of water to flow through said support.

22. A process as claimed in claim 21 wherein:
said solution is sufficiently dilute so that there is substantially no chance of said prepolymer chains reacting until the solvent content of said solution is reduced.

23. A process as claimed in claim 21 wherein:
said polymer chains are capable of reacting to form a polymer selected from the group consisting of epoxy and phenolic polymers.

24. A process of producing a reverse osmosis membrane which comprises:

forming a porous, sheet-like support layer which is sufficiently porous so that water can pass through said support layer,

forming a continuous hydrogel layer upon a surface of said support layer in such a manner that the pores of said support layer are sufficiently free from the presence of material from within said hydrogel layer so that fluid flow through the pores of said support layer is not detrimentally affected by the presence of said material within said pores, and

forming a continuous active layer capable of dissolving water so as to segregate the dissolved water from other materials in the solution being purified on the surface of said hydrogel layer remote from said support layer.

25. A process as claimed in claim 24 wherein:
all of said layers are formed of polymer compositions, and

the formation of at least one of said layers includes the step of cross-linking said one of said layers with an adjacent layer during the formation of said one of said layers.

26. A process as claimed in claim 24 wherein:
said hydrogel layer and said active layer are concurrently formed by applying to a surface of said support layer a solution containing both swollen hydrogel polymer coils and materials necessary for the production of said active layer and then heating so as to volatilize the solvent from said solution and so as to concurrently produce said hydrogel and active layers by entropic separation.

27. A reverse osmosis membrane comprising
a) an active layer consisting essentially of a continuous, non-porous, uniform film of an organic, film-forming polymer which is substantially inert in the presence of an oxidizing agent having a sufficient oxidizing potential to serve as a sterilizing agent, said film being from about 50 to about 1500 Å thick and being capable of dissolving an amount of water equal to at least two percent by weight of the weight of the film; and

b) a physical support for said active layer, said physical support comprising a highly asymmetric polymeric membrane containing a skin and a porous substructure, said skin containing pores which have an average pore diameter of from about 0.005 to about 3.0 microns and said substructure comprising a reticulated structure

which contains pores which have an average pore diameter of from about 10 to about 20,000 times as large as the average pore diameter of the pores of said skin, the pores of the support increasing gradually in size from the skin to the face of the membrane opposite the skin.

28. The reverse osmosis membrane of Claim 27 further including

(c) a continuous, non-porous layer of an irreversible hydrogel composition containing at least one hydrogel-forming polymer and water, said hydrogel layer being located between said support and said active layer.

CLAIMS SUPPORTED BY THE SUPPLEMENTARY DISCLOSURE

29. The membrane of Claim 1 wherein said active layer film forming polymer is cellulose triacetate.

30. The membrane of Claim 1 wherein said membrane includes a continuous, non-porous layer of a thermally irreversible hydrogel composition containing at least one hydrogel-forming polymer and water, said hydrogel layer being located between said support and said active layer, and said film-forming polymer is cellulose triacetate.

31. The membrane of Claim 1 wherein said membrane includes a continuous, non-porous layer of a thermally irreversible hydrogel composition containing at least one hydrogel-forming polymer and water, wherein said hydrogel layer is located between said support and said active layer, and is from about 2 to about 3 microns thick when dry, said polymer in said hydrogel layer is capable of absorbing an amount of water equal to at least 15 times the weight of said hydrogel-forming polymer and is incapable of absorbing an amount of water in excess of about 200 times of its own weight, said hydrogel-forming polymer in said hydrogel layer is present in the form of swollen polymer coils of polymer chains having a molecular weight of from about 500,000 to about 3,000,000, said film-forming polymer is cellulose triacetate and is capable of absorbing an amount of water equal to from about 5 to about 15 percent of its own dry weight, said film is from about 200° to about 500°A thick, said support is a porous asymmetric member having a porous surface in contact with said hydrogel layer, the porosity of said asymmetric member increasing in accordance with the distance away from said hydrogel layer, from about 10 to about 30 percent of the surface of said support in contact with said hydrogel layer is open and from about 70 to about 95 percent of the surface of said support remote from said hydrogel layer is open, the pores within said porous support in contact with said hydrogel layer are from about 0.5 to about 5 microns in diameter, and the pores in said surface in contact with said hydrogel layer are substantially free from material from within said hydrogel layer.

32. The membrane of Claim 1 wherein said active layer is made of cellulose triacetate and said physical support is made of polyvinylidene fluoride.

33. A reverse osmosis membrane comprising

(a) an active layer consisting essentially of a continuous, non-porous, uniform film of an organic, film-forming polymer which is substantially inert in the presence of an oxidizing agent having a sufficient oxidizing potential to serve as a sterilizing agent, said film being from about 50 to about 1500°A thick and capable of absorbing an amount of water equal to at least about two percent by weight of the dry weight of the film,

(b) a physical support for said active layer, said physical support comprising a polyvinylidene fluoride membrane containing a skin and a porous substructure, said skin containing pores which have an average pore diameter of from about 0.005 to about 3.0 microns and said substructure comprising a reticulated structure which contains pores which have an average pore diameter of from about 10 to about 20,000 times as large as the average pore diameter of the pores of said skin, said membrane having a bulk porosity greater than about 70%, and

(c) a continuous, non-porous layer of an irreversible hydrogel composition containing at least one hydrogel-forming polymer and water, said hydrogel layer being located between said support and said active layer.

34. A reverse osmosis membrane comprising

(a) an active layer consisting essentially of a continuous, non-porous film of cellulose triacetate, said film being from about 50 to about 1500°A thick and being capable of absorbing an amount of water equal to at least about two percent by weight of the dry weight of the film, and

(b) a physical support for said active layer wherein said physical support is made of polyvinylidene fluoride.

35. A reverse osmosis membrane comprising

(a) an active layer consisting essentially of a continuous non-porous film of cellulose triacetate, and

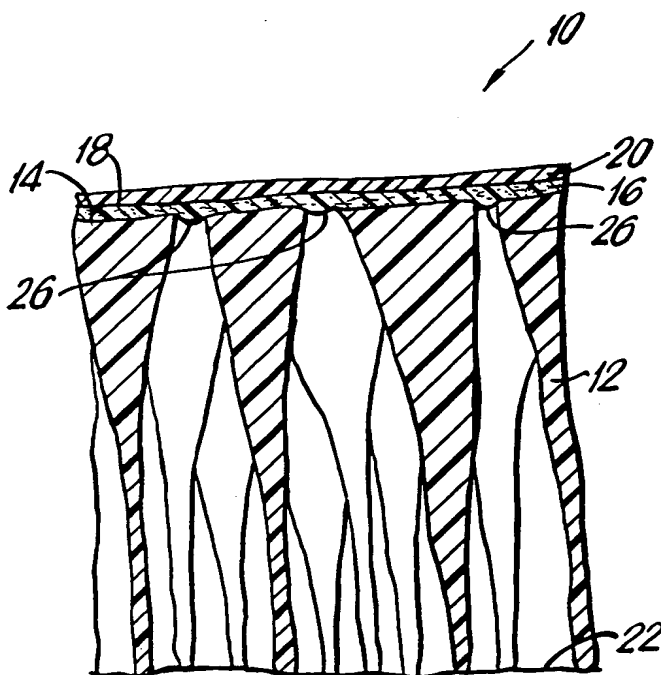
(b) a physical support for said active layer, said physical support consisting essentially of polyvinylidene fluoride.

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36. The process of Claim 21, 22 or 24, wherein said porous support is made of polyvinylidene fluoride and said active layer is made of cellulose triacetate.



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